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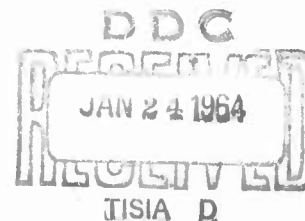
MOLECULAR STRUCTURE AND MATERIALS CHARACTERIZATION

TECHNICAL DOCUMENTARY REPORT No. RTD-TDR-63-4104

NOVEMBER 1963

AF MATERIALS LABORATORY
RESEARCH AND TECHNOLOGY DIVISION
AIR FORCE SYSTEMS COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OHIO

Project No. 7360, Task No. 736005



(Prepared under Contract No. AF 33(616)-8465 by
Monsanto Research Corporation, Dayton, Ohio; J. E. Katon, Author)

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FOREWORD

This report was prepared by Monsanto Research Corporation under USAF Contract No. AF 33(616)-8465. This contract was initiated under Project No. 7360, "The Chemistry and Physics of Materials", Task No. 736005, "Compositional, Atomic and Molecular Analysis". The work was administered under the direction of the AF Materials Laboratory, Research and Technology Division, Wright-Patterson Air Force Base, Ohio, with Mr. F. F. Bentley as project engineer.

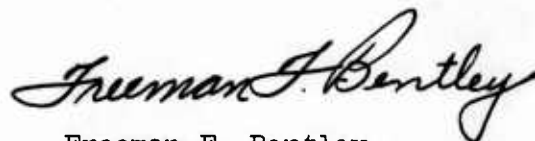
This report summarizes work carried out from 1 July 1962 to 1 July 1963.

The work was performed at the Dayton Laboratory of Monsanto Research Corporation. The major participants were Messrs. F. N. Hodgson, I. O. Salyer, H. S. Wilson, W. R. Feairheller, J. V. Pustinger, and W. D. Ross and Drs. J. E. Katon and W. G. Scribner. Dr. J. E. Katon served as project leader.

ABSTRACT

Research on the determination of molecular structures, characterization of materials, and the development and application of various analytical techniques, and various services supplied the Air Force in support of in-house programs, during the period 1 July 1962 - 1 July 1963 is summarized. The three research projects, reported in detail elsewhere, concern infrared spectra/structure correlations of aliphatic monocarboxylic acids and organosulfur compounds; solid state mass spectrometric studies; and the characterization of polyurethane elastomers with special reference to those used as binders for solid propellants.

This technical documentary report has been reviewed and is approved.



Freeman F. Bentley
Chief, Analytical Branch
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I. INTRODUCTION

This report summarizes the progress under contract number AF 33(616)-8465 during the period 1 July 1962 - 1 July 1963. The prime goal of the program is the study of molecular structure and materials characterization. In addition, various services to support in-house programs at RTD are provided.

The molecular structure and materials characterization portion of the program comprised three separate projects: vibrational spectroscopy, mass spectroscopy, and characterization of polyurethane elastomers used as binders for solid propellant grains. The fundamental knowledge gained can be applied to development of new techniques and procedures for characterizing and analyzing new research materials that R and D programs generate.

Diverse service functions were performed, ranging from routine analyses to the development of an analytical method for a new material, or even the synthesis of model compounds for comparison purposes. Since these services may bring to light certain new techniques or information, they are reported in some detail.

All the research projects and service work has been reported previously or is being reported concurrently. This report briefly summarizes the results of these projects, therefore, and refers to the individual reports for a detailed description of the goals, procedures, techniques, results, and conclusions.

II. DISCUSSION

A. VIBRATIONAL SPECTROSCOPY (Ref. 1)

Our research on vibrational spectroscopy concerns primarily infrared spectra-structure correlations in the $700\text{-}300\text{ cm}^{-1}$ region. Work is carried out in higher frequency regions, however, when desirable. The latter situation arises in regard to particular classes of compounds which have not been thoroughly investigated in these higher frequency regions. The utility of the higher frequency region in determining molecular structures is well-known, and recently the utility of the lower frequency region in the same regard has been illustrated with ketones (Ref. 2) and aldehydes (Ref. 3).

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We have now completed a study of the infrared spectra of aliphatic monocarboxylic acids in the 700-300 cm^{-1} region in the liquid and solid states. The liquid state spectra allow differentiation between α -branched and non- α -branched compounds. The solid state spectra of the normal compounds are very specific below 500 cm^{-1} and can be used to determine chain length of an unknown acid.

Tentative assignment for three fundamental vibrations in the 700-300 cm^{-1} region in acids has been made. A complex of bands in the 600-700 cm^{-1} region has been assigned as due to the CO_2 in-plane bending motion. The detailed structure of this complex appears to be a sensitive function of the degree and/or strength of association between the molecules. Two bands, which are usually only partially resolved from each other, occur near 500 cm^{-1} . One of these has been assigned as a CCO in-plane bending motion and the other as the CO_2 out-of-plane bending motion. The frequency of both of these vibrations is sensitive to α -substitution. A spectra-structure correlation chart for this class of compounds is given in Fig. 1.

The study of organosulfur compounds was somewhat limited by a scarcity of compounds. Little new information was obtained in regard to these compounds except in the specific case of sulfones. The spectra of a number of aromatic sulfones in the higher frequency region are available in the literature and correlations have been made (Ref. 4). We have investigated a number of aliphatic sulfones and find that these previous correlations are not generally applicable. In addition, the effect of physical state on the spectra is not the same with the aliphatic sulfones as with the aromatic compounds.

In the low frequency region it was found that all sulfones have a band at 548-610 cm^{-1} and those which do not contain unsaturation have an absorption at 495-520 cm^{-1} . As an aid to assignment and understanding the vibrations of complex sulfones, the vibrational assignment of dimethyl sulfone, which has not been previously assigned, is underway.

Tentative spectra-structure correlation charts for organosulfur compounds are presented in Figs. 2 and 3.

B. MASS SPECTROMETRY

The research in mass spectrometry this year involved a number of projects related to the mass spectra of solids. In addition, a number of methods and techniques were studied.

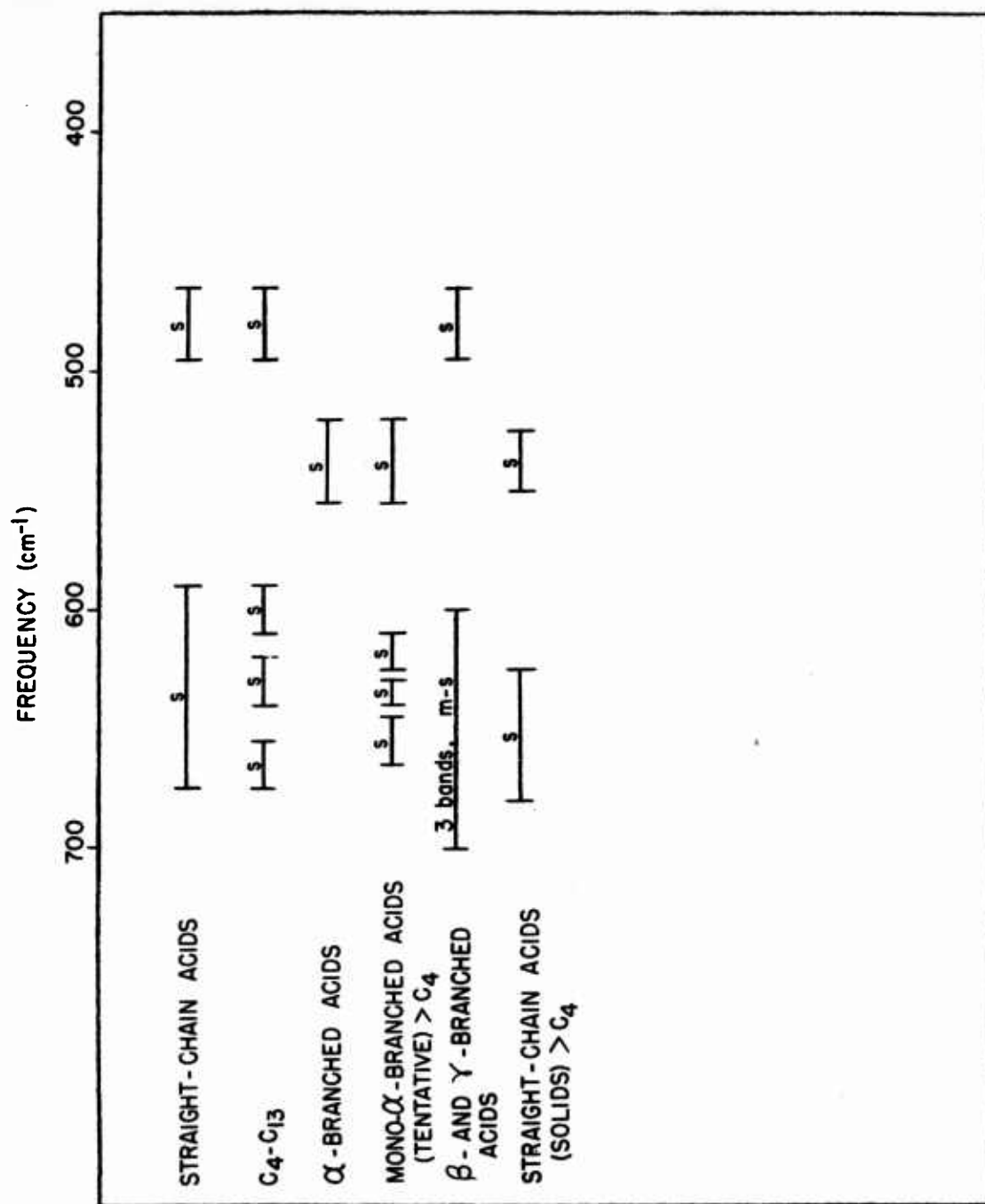


Figure 1. Spectra-structure correlation chart for aliphatic monocarboxylic acids

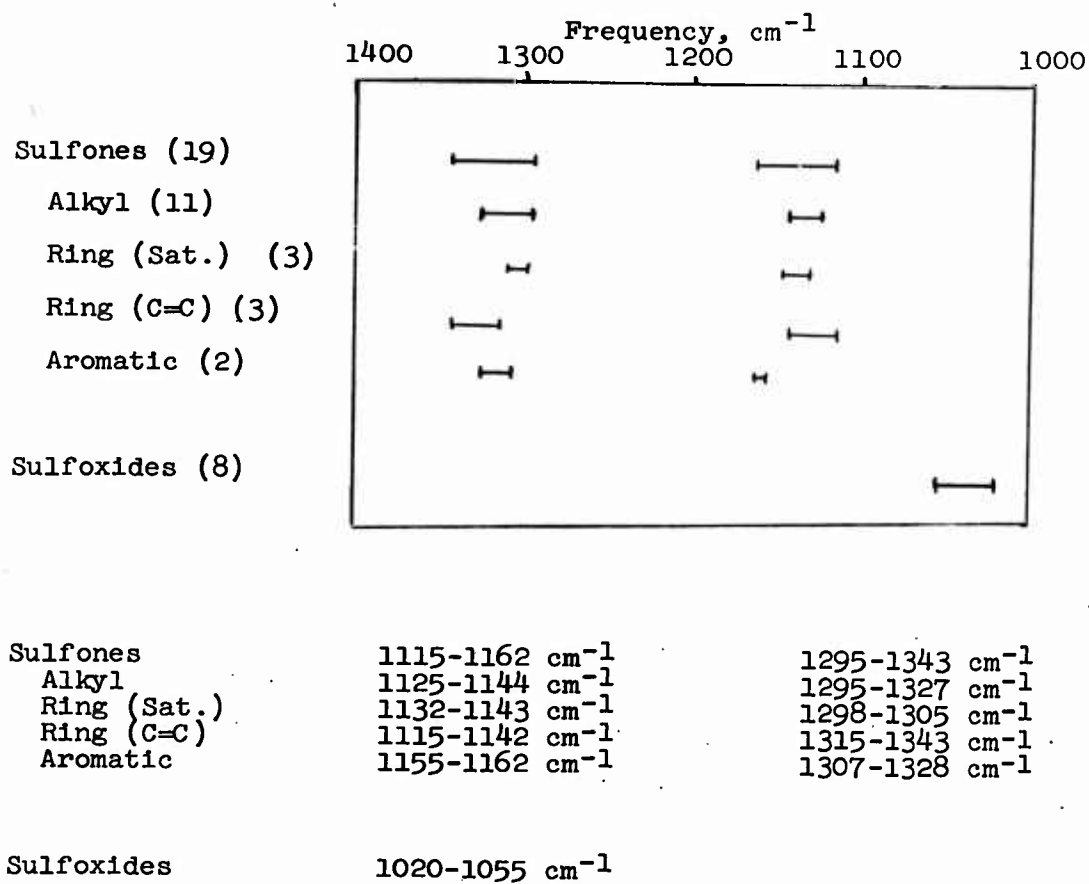
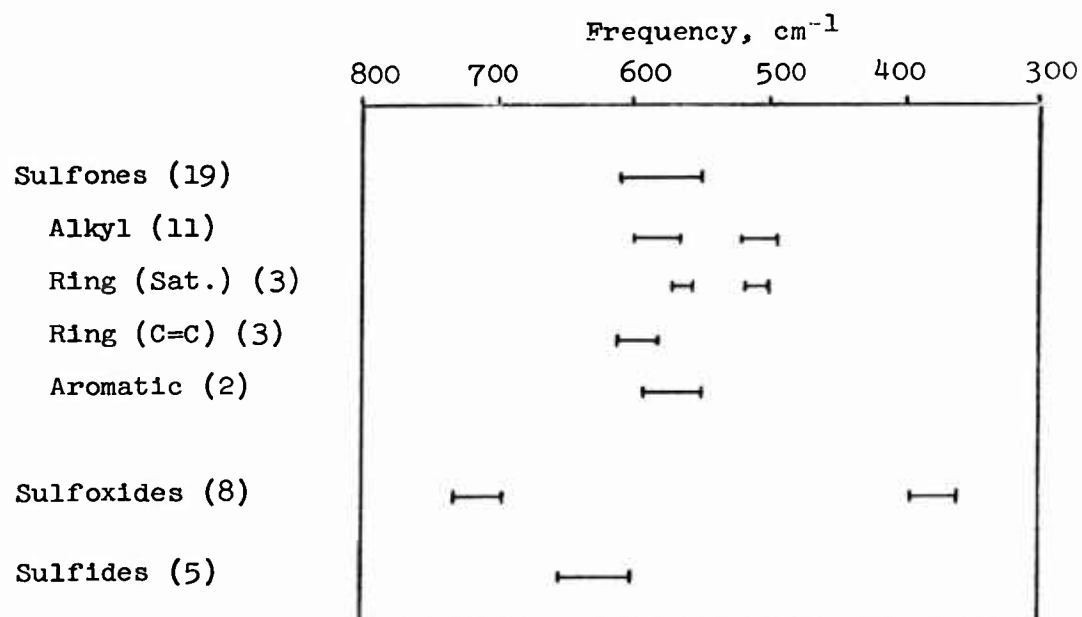


Figure 2. Correlation chart - sulfur compounds high frequency region



Sulfones	548-610 cm^{-1}	
Alkyl	565-599 cm^{-1} (m-s)	495-520 cm^{-1} (m-s)
Ring (Sat.)	555-570 cm^{-1} (s)	500-517 cm^{-1} (m-s)
Ring (C=C)	580-610 cm^{-1} (s)	
Aromatic	548-592 (2 bands) (s)	
Sulfoxides	698-730 (s)	360-395 (variable)
Sulfides	602-655 cm^{-1} (m-s)	

Figure 3. Correlation chart - sulfur compounds low frequency region

Molecular carbon species present in the vacuum spark of the mass spectrograph were studied for various forms of carbon. Included were graphite, diamond, amorphous carbon, and carbides. Each form shows a unique carbon association pattern.

Special techniques were developed to run volatile samples, to ionize gases in the spark source, and to produce a mass reference plate based on spark spectra containing combinations of carbon and hydrogen.

A method for quantitative determination of impurities in solids was devised and is illustrated by a determination of oxygen in beryllium. These results were compared with data from various other techniques performed at other, independent laboratories.

C. POLYMER CHARACTERIZATION (Ref. 6)

One requirement for satisfactory performance of solid propellants is storage stability. Previous malfunctions due to storage instability have given some indication that the source of the problem was the polyurethane binder. We have, therefore investigated the physical and thermal properties of intermediate molecular weight materials prepared from propellant binder raw materials and of elastomer formulations which are chemically similar to the actual propellant.

Included in the study were the chemical reaction variables in the synthesis of the elastomers; formulation variables such as catalyst type, atmosphere, oxidant, and moisture absorption; thermogravimetric analysis and differential thermal analysis of the materials prepared; various polymer properties such as tensile strength, glass transition temperatures, density, and elongation; and infrared spectral and nuclear magnetic resonance characteristics of the various linkages found in polyurethanes.

The results led to the following conclusions:

1. Present polyurethane propellant binders are only marginal with respect to thermal stability and physical properties.
2. Present catalysts and curing cycles used in the manufacture of polyurethane propellant binders may not lead to complete reaction of the starting isocyanate even when mixing is known to be uniform.
3. Excess or unreacted isocyanates are a potential or actual hazard to polyurethane propellant binder stability, especially at the elevated temperatures encountered during firing.

It has been found that polyurethane elastomers can be characterized, at least in part, by infrared spectroscopy using attenuated total reflectance techniques. This technique has been shown to be applicable to the determination of the presence of certain linkages which affect the stability of the binder.

D. SERVICE AND SUPPORT

Various small tasks have been undertaken to support ASD in-house projects or to augment Air Force facilities in periods of heavy workload. In addition to routine analytical service, other services requiring equipment and experience not otherwise available to the Air Force are sometimes furnished.

1. Method Development

The determination of the molecular weight distribution of high polymers by elution fractionation is a well-known technique. The standard method, however, is not applicable to all polymer samples, having been devised for the simple polymeric systems that are conventionally synthesized. While attempting to characterize an Air Force sample of polystyrene it was found that the standard procedure was inapplicable. The Air Force sample was a synthesized binodal, made by mixing two closely spaced monodispersed samples of ionically initiated polystyrene. Since the molecular weight distribution of this polymer was needed, the standard elution fractionation technique was modified, tested, and the modified method was applied to these binodal samples. The procedures and results have been reported in detail (Ref. 7).

The determination of particle characteristics (size, shape, etc.) by electron microscopy is a common procedure. The preparation of the sample prior to study is, however, highly dependant on the nature of the material and the quality of the results may depend strongly on the preparative method used.

Several sample preparation techniques were compared, using experimental greases developed by the Air Force. The procedure involves using the various sample preparation techniques on a given sample followed by electron microscopic investigation of the sample and comparison of the electron photomicrographs. The details of the various procedures and the results have been reported (Ref. 8).

2. Analytical Support

Summarized below are the routine and semiroutine analyses that were carried out.

<u>Method</u>	<u>No. of Analyses</u>
Mass Spectrometry	31
Emission Spectrometry	22
X-ray Diffraction	7
Infrared Spectrometry	4
Microanalyses	102
Nuclear Magnetic Resonance Spectrometry	51
Electron Microscopy	16
Gas-Liquid Chromatography	17
Preparative Gas-Liquid Chromatography	6
Miscellaneous	44
Total	300

The individual procedures and results have been reported previously (Ref. 9).

3. Synthesis

Four alkyl bromides needed as model compounds for research projects were synthesized. The same general reaction was used for the four compounds, and is represented by the equation: $\text{ROH} + \text{HBr} \longrightarrow \text{RBr} + \text{H}_2\text{O}$.

2-Bromo-2-methylhexane Anhydrous HBr was passed into 50 g (0.43 mole) of redistilled 2-methyl-2-hexanol (b.p. $143^\circ\text{C}/\text{atm}$, $n_D^{25} 1.4163$) cooled in an ice bath, until the theoretical weight increase was observed. A second phase (H_2O) formed during the process.

The mixture was washed with ice water, cold 5% sodium carbonate and again with ice water. After initial drying with sodium sulfate, the product was further dried over magnesium sulfate. Distillation gave an 86% yield of 2-bromo-2-methylhexane, b.p. $54^\circ\text{C}/20 \text{ mm}$, $n_D^{25} 1.4461-64$. VPC showed two small impurities with a total area of 7.6%.

3-Bromo-3-methylhexane 3-Methyl-3-hexanol (46 g), $n_D^{25} 1.4210$, was treated as in the previous experiment. Distillation gave 47 g, $n_D^{25} 1.4416-1.4529$. Redistillation gave 18.5 g, b.p. $55^\circ\text{C}/20 \text{ mm}$, $n_D^{25} 1.4518-21$. By VPC this sample was better than 95% pure.

3-Bromo-3,4-dimethylhexane 3,4-Dimethyl-3-hexanol, 26 g, (as received, Columbia Organic Chemical Corp., $n_D^{25} 1.4331$) was treated with anhydrous HBr. The washed product was dried over calcium chloride, then over calcium sulfate, and stored in a desiccator over sodium hydroxide for two days to absorb HBr.

Distillation gave 23 g of 3-bromo-3,4-dimethylhexane, b.p. 43°C/3 mm, n_D^{25} 1.4635 (60% yield).

3-Bromo-3,5-dimethylhexane Redistilled 3,5-dimethyl-3-hexanol (b.p. 90°C/85 mm, n_D^{25} 1.4246) was treated with HBr, then was washed, dried, and distilled, to give a 45% yield of 3-bromo-3,5-dimethylhexane, b.p. 63°C/13 mm, n_D^{25} 1.4531.

E. PUBLICATIONS, PAPERS, AND REPORTS

During the period 1 July 1962 - 1 July 1963 the following publications, papers and reports based on work performed under this contract were published or presented.

1. W. L. Baun, F. N. Hodgson, and M. Desjardins, "Mass Spectrographic Measurement of Molecular Carbon Species from a Radio Frequency Spark", Rocky Mountain Spectroscopy Symposium, Denver, 6-7 August 1962.
2. F. N. Hodgson, M. Desjardins, and W. Baun, "Elemental Associations Observed in the Radio-Frequency Spark Source", ASTM Committee E-14 on Mass Spectrometry, San Francisco, 19 May 1963.
3. J. E. Katon and F. F. Bentley, "New Spectra-Structure Correlations of Ketones in the 700-350 cm^{-1} Region", Spectrochim. Acta 19, 639 (1963).
4. W. L. Baun, F. N. Hodgson, and M. Desjardins, "Mass Spectrographic Study of Molecular Carbon Ions Found in a Spark Source", J. Chem. Phys. 38, 2787 (1963).
5. F. N. Hodgson, M. Desjardins, and W. L. Baun, "A Study of Polynuclear Aromatic Hydrocarbons Using the Vacuum Spark Mass Spectrograph", J. Phys. Chem. 67, 1250 (1963).
6. J. E. Katon, "The Infrared Spectra of Selected Ketones, Ethers and Alcohols Between 15 and 35 Microns", ASD-TDR-62-743 (August 1962).
7. J. V. Pustinger and J. E. Katon, "The Infrared Spectra of Some Aldehydes Between 15 and 35 Microns", ASD-TDR-62-862 (October 1962).
8. J. E. Katon, "Annual Summary Report on Molecular Structure and Materials Characterization", ASD-TDR-62-940 (November 1962).

9. F. N. Hodgson, M. Desjardins, and W. L. Baun, "Spark Source Mass Spectrometry of Organic Compounds", ASD-TDR-63-383 (June 1963).

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6. Wilson, H. S., Salyer, I. O. and Katon, J. E., "Polyurethane Propellant Binder Characterization", Summary Technical Report No. 8, AF 33(616)-8465.
7. Analysis Report 20, AF 33(616)-8465.
8. Analysis Report 63, AF 33(616)-8465.
9. Analysis Report 4-19, 21-62, 64-66, AF 33(616)-8465.

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